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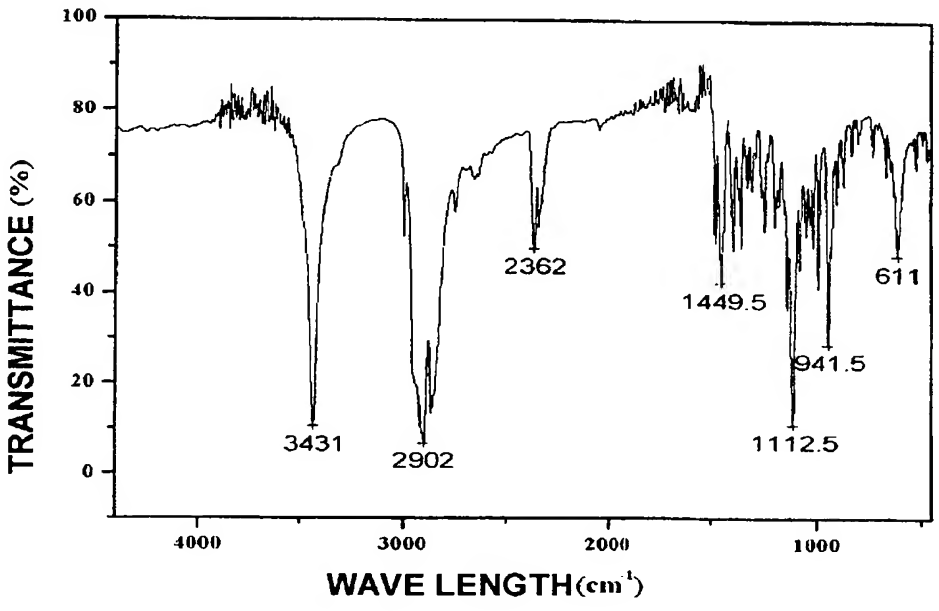
(54) Title: 2-ALKOXYALKYL-2-ADAMANTYL (METH)ACRYLATE AND METHOD FOR PREPARING SAME



(57) Abstract: 2-Alkoxyalkyl-2-adamantyl (meth)acrylate and a method for preparing same are provided.

WO 03/104182 A1

2-ALKOXYALKYL-2-ADAMANTYL (METH)ACRYLATE AND METHOD FOR PREPARING SAME

Field of the Invention

The present invention relates to a novel adamantane derivative, 2-alkoxyalkyl-2-adamantyl (meth)acrylate, and a method for preparing same.

Background of the Invention

Adamantane derivatives having a vinyl substituent have been used in the production of photocurable resins having excellent optical and mechanical properties suitable for applications in such fields as adhesive, printing ink, photosensitive resin, and optical fiber coat. For example, Japanese Laid-open Patent Publication No. Hei9-73173 discloses 2-adamantyl (meth)acrylate useful for the production of chemical amplification resist; and European Laid-open Patent Publication No. 1 000 924 A1, an acid-sensitive polymer having adamantyl moieties which has sufficiently high etching resistance for providing a finer line pattern.

Adamantyl derivatives have also been used as drug intermediates. For example, US. patent No. 6,127,415 discloses apoptosis-inducing adamantyl derivatives and their usage as antitumor agents; and Korean Laid-open Patent Publication No. 1997-42511, a pharmaceutical composition comprising an adamantyl derivative which is active against dermatological diseases.

Summary of the Invention

Accordingly, it is an object of the present invention to provide a novel adamantane derivative which is useful as a monomer for the production of a photocurable resin or as a drug intermediate.

It is another object of the present invention to provide a method for preparing the adamantine derivative.

Brief Description of the Drawings

The above and other objects and features of the present invention will become apparent from the following description of the invention taken in conjunction with the following accompanying drawings, which respectively show:

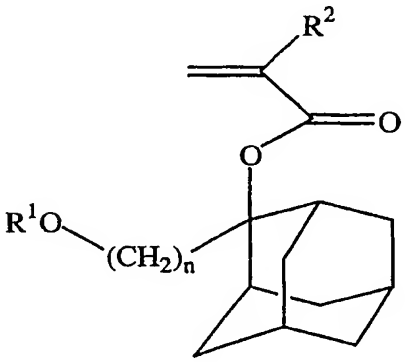
FIG. 1 : an FT-IR spectrum of 2-(4-methoxybutyl)-2-adamantanol produced in Example 1 of the present invention;

FIG. 2 : an NMR spectrum of 2-(4-methoxybutyl)-2-adamantyl acrylate produced in Example 1 of the present invention; and

FIG. 3 : an NMR spectrum of 2-(4-methoxybutyl)-2-adamantyl methacrylate produced in Example 2 of the present invention.

Detailed Description of the Invention

In accordance with one aspect of the present invention, there is provided 2-alkoxyalkyl-2-adamantyl (meth)acrylate represented by the following formula I:



(I)

wherein, R^1 is hydrogen, C_{1-4} alkyl or C_{3-8} cycloalkyl; R^2 is hydrogen or methyl; and n is an integer.

Preferably, R^1 is methyl and n is an integer in the range of 1 to 4.

The inventive 2-adamantyl (meth)acrylate is useful as a resist material suitable for short-wave exposure source (ArF excimer laser) since it is an acid-sensitive compound containing an alkali-soluble group protected with an alicyclic hydrocarbon group.

In accordance with another aspect of the present, there is provided a method of preparing the compound of formula I comprising:

a) reacting 2-adamantanone with a Grignard reagent of formula $R^1O(CH_2)_nMgX$ to obtain a 2-alkoxyalkyl-2-adamantanol, the alkoxyalkyl being $R^1O(CH_2)_n$-; and

b) reacting the 2-alkoxyalkyl-2-adamantanol with (meth)acryloyl chloride to obtain 2-alkoxyalkyl-2-adamantyl (meth)acrylate, wherein X is chlorine or bromine.

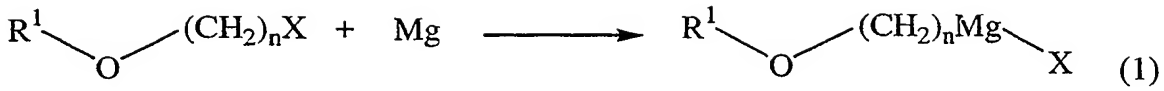
Preferably, step b) is performed in the presence of a basic reagent.

In accordance with a preferred embodiment of the present invention, the method of preparing the compound may further comprise a step of reacting alkoxyalkyl halide with magnesium to obtain alkoxyalkyl Grignard reagent before step a).

In the preparation method of the compound according to the present invention, a separation process may be performed after each step is completed. However, the separation process may be performed after all steps are performed in situ. Accordingly, synthesized Grignard reagent may be employed in step a) without further separation.

A process for producing 2-alkoxyalkyl-2-adamantyl (meth)acrylate according to the present invention will now be described in detail.

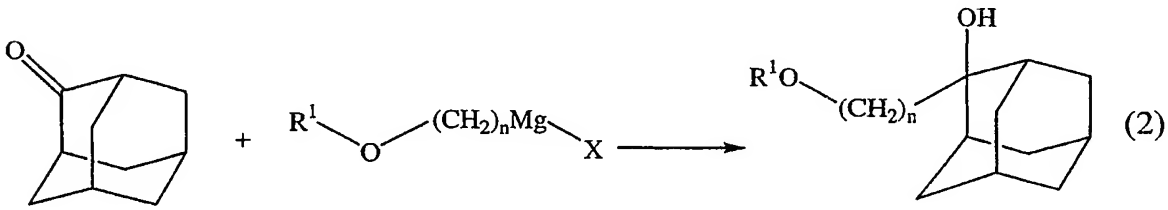
As shown in reaction scheme (1), an alkoxyalkyl halide is reacted with magnesium to synthesize an alkoxyalkyl magnesium halide (an alkoxyalkyl reagent):



(1)

wherein, R^1 is hydrogen, C_{1-4} alkyl or C_{3-8} cycloalkyl; X is Cl or Br; and n is an integer.

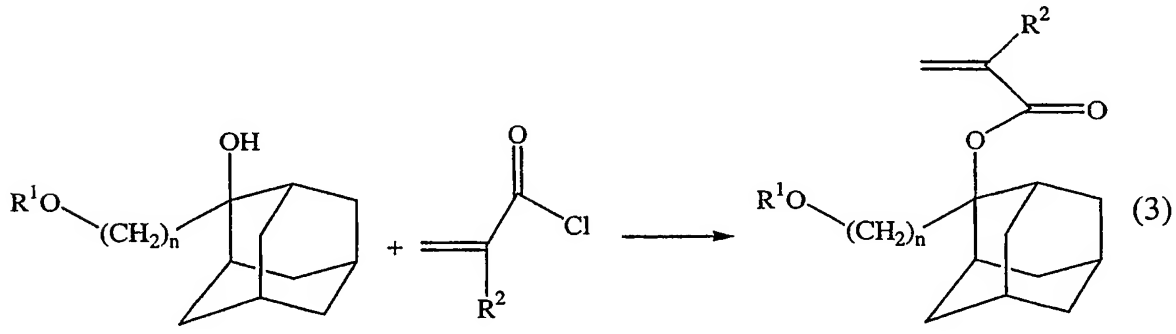
Next, as shown in reaction scheme (2), adamantanone and the alkoxyalkyl Grignard reagent are reacted, to synthesize a 2-alkoxyalkyl-2-adamantanol:



(2)

wherein, R^1 and n are the same as defined above.

Finally, as shown in reaction scheme (3), the 2-alkoxyalkyl-2-adamantanol is reacted with acryloyl or methacryloyl chloride to obtain 2-alkoxyalkyl-2-adamantyl (meth)acrylate:



(3)

wherein, R^1, R^2 and n are the same as defined above.

The alkoxyalkyl Grignard reagent is employed preferably in an amount ranging from 1.2 to 2.0 equivalents based on the amount of 2-adamantanone, and (meth)acryloyl chloride is employed preferably in an amount ranging from 1.2 to

2.0 mole per mole of 2-alkoxyalkyl-2-adamantanol.

Preferably, the basic reagent that may be used in the present invention is a tertiary amine such as triethyl amine or pyridine and is employed in an amount ranging from 1.4 to 2.2 mole per mole of 2-alkoxyalkyl-2-adamantanol.

In accordance with a preferred embodiment of the present invention, the reaction for synthesizing 2-alkoxyalkyl-2-adamantanol is performed at a temperature ranging from –20 to 0℃, for a period ranging from 2 to 3 hours; and the reaction for synthesizing 2-alkoxyalkyl-2-adamantyl (meth)acrylate, at a temperature ranging from –20 to 0℃, for a period ranging from 2 to 15 hours.

The present invention is described in more detail below by referring to the following Examples, and the Examples are given for the purpose of illustration only, and are not intended to limit the scope of the invention.

Example 1: Preparation of 2-(4-methoxybutyl)-2-adamantyl acrylate

A. Synthesis of 4-methoxybutyl magnesium chloride (4-methoxybutyl Grignard reagent)

52 g of 4-methoxy-1-butanol (0.5 mol) and 40 g of pyridine (0.5 mol) were placed into a 1 liter three-necked flask and then cooled to 0℃. Thionyl chloride (119 g, 1.0 mol) was added slowly thereto using a dropping funnel. The mixture was refluxed for about 1 hour, after poured into water to destroy completion of the reaction, excess thionyl chloride extracted with 300 ml of methylene chloride. Then, the organic layer was washed with 5% sodium hydroxide and dried over magnesium sulfate to obtain 4-methoxybutyl chloride (yield: 80%).

26.7 g of magnesium turnings (1.1 mol) was dispersed in 500ml of anhydrous THF, and then, a small amount of iodine and a drop of 4-methoxybutyl chloride were added thereto, followed by heating up to 40℃ to activate magnesium. After the color of the solution changed from brown to colorless, the mixture was cooled and then 108.57 g of the 4-methoxybutyl

chloride (1.0 mol) was added slowly thereto. After completion of the addition, the reaction mixture was warmed, and refluxed for about 1 hour to obtain a 4-methoxybutylmagnesium chloride solution.

B. Synthesis of 2-(4-methoxybutyl)-2-adamantanol

The 4-methoxybutylmagnesium chloride solution obtained in step A in an amount corresponding to 1.0 mole of 4-methoxybutyl chloride was placed in a 1 liter flask using a cannular and cooled to 0℃. 120.17 g of 2-adamantanone (0.8 mol) was added slowly thereto using a dropping funnel, and stirred at room temperature for about 12 hours. After completion of the reaction, excess THF was removed using a rotary evaporator, the resulting residue was poured into water, the solution was neutralized with dilute sulfuric acid, extracted using diethyl ether, and dried over magnesium sulfate. The crude product was re-crystallized from n-hexane-methylene chloride to obtain 2-(4-methoxybutyl)-2-adamantanol (yield: 80 %).

FT-IR (KBr; cm^{-1}): 3431, 2902, 1449.5, 1112.5, 941.5, 611.

C. Synthesis of 2-(4-methoxybutyl)-2-adamantyl acrylate

44.87 g of the 2-(4-methoxybutyl)-2-adamantanol (0.2 mol) obtained in step B and 32.38 g of triethylamine (0.32 mol) were dissolved in 300 ml of THF and then 25.34 g of acryloyl chloride (0.28 mol) was added slowly thereto using a dropping funnel. Then, the reaction was stirred at room temperature for about 12 hours.

After completion of the reaction, excess THF was removed using a rotary evaporator, and the resulting mixture was poured into water. The solution was neutralized with dilute sulfuric acid, extracted using diethyl ether, and the ether layer was dried over magnesium sulfate. After removing diethyl ether, the crude product was vacuum distilled to obtain 2-(4-methoxybutyl)-2-adamantyl acrylate (yield: 80%).

^{1}H-NMR ($CDCl_3$; ppm): 6.25(1H, d), 6.1(1H, dd), 5.9(1H, d), 3.3(2H, t),

3.2(3H, S), 2.3-1.2(m).

Example 2: Preparation of 2-(4-methoxybutyl)-2-adamantyl methacrylate

The title compound was prepared in the same manner as in Example 1, except that 29.27 g of methacryloyl chloride (0.28 mol) was used instead of 25.34 g of acryloyl chloride (yield: 85%).

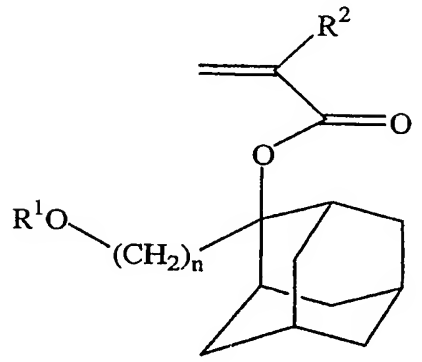
H-NMR ($CDCl_3$; ppm): 6.1(1H, d), 5.5(1H, d), 3.3(2H, t), 3.2(3H, S), 2.3-1.2(m).

2-Alkoxyalkyl-2-adamantyl (meth)acrylate according to the present invention can be used for various applications e.g. as a monomer of a photocurable resin, a drug intermediate and the like. Also, the inventive method for preparing 2-alkoxyalkyl-2-adamantyl (meth)acrylate is simple, a high yield process suitable for commercial-scale production.

While the invention has been described with respect to the above specific embodiments, it should be recognized that various modifications and changes may be made to the invention by those skilled in the art which also fall within the scope of the invention as defined by the appended claims.

What is claimed is :

1. A compound of formula I:



(I)

wherein, R^1 is hydrogen, C_{1-4} alkyl or C_{3-8} cycloalkyl; R^2 is hydrogen or methyl; and n is an integer.

2. The compound of claim 1, wherein n is an integer in the range of 1 to 4.

3. A method of preparing the compound of claim 1, comprising:

a) reacting 2-adamantanone with a Grignard reagent of formula $R^1O(CH_2)_nMgX$ to obtain a 2-alkoxyalkyl-2-adamantanol, the alkoxyalkyl being $R^1O(CH_2)_n$-; and

b) reacting the 2-alkoxyalkyl-2-adamantanol with (meth)acryloyl chloride to obtain 2-alkoxyalkyl-2-adamantyl (meth)acrylate, wherein X is chlorine or bromine.

4. The method of claim 3, wherein step b) is performed in the presence of a basic reagent.

5. The method of claim 3, wherein in step a) 2-alkoxyalkyl-2-adamantanol is 2-(4-methoxybutyl)-2-adamantanol.

FIG. 1

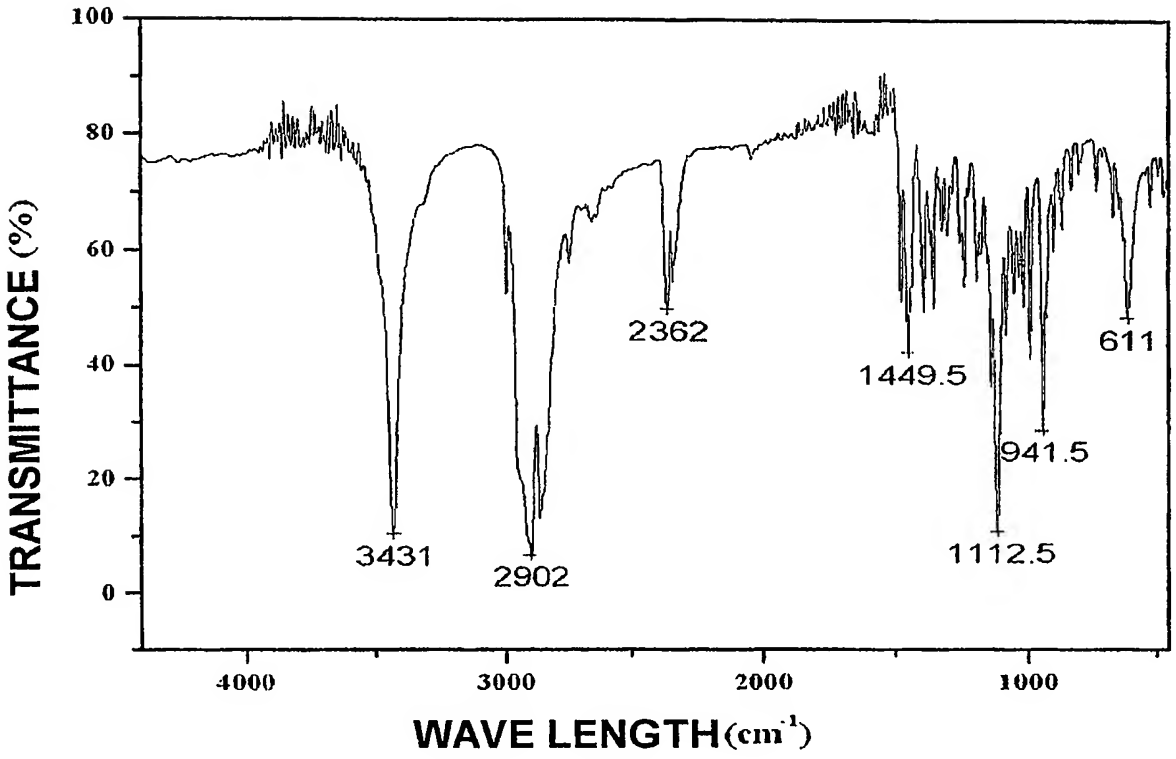


FIG. 2

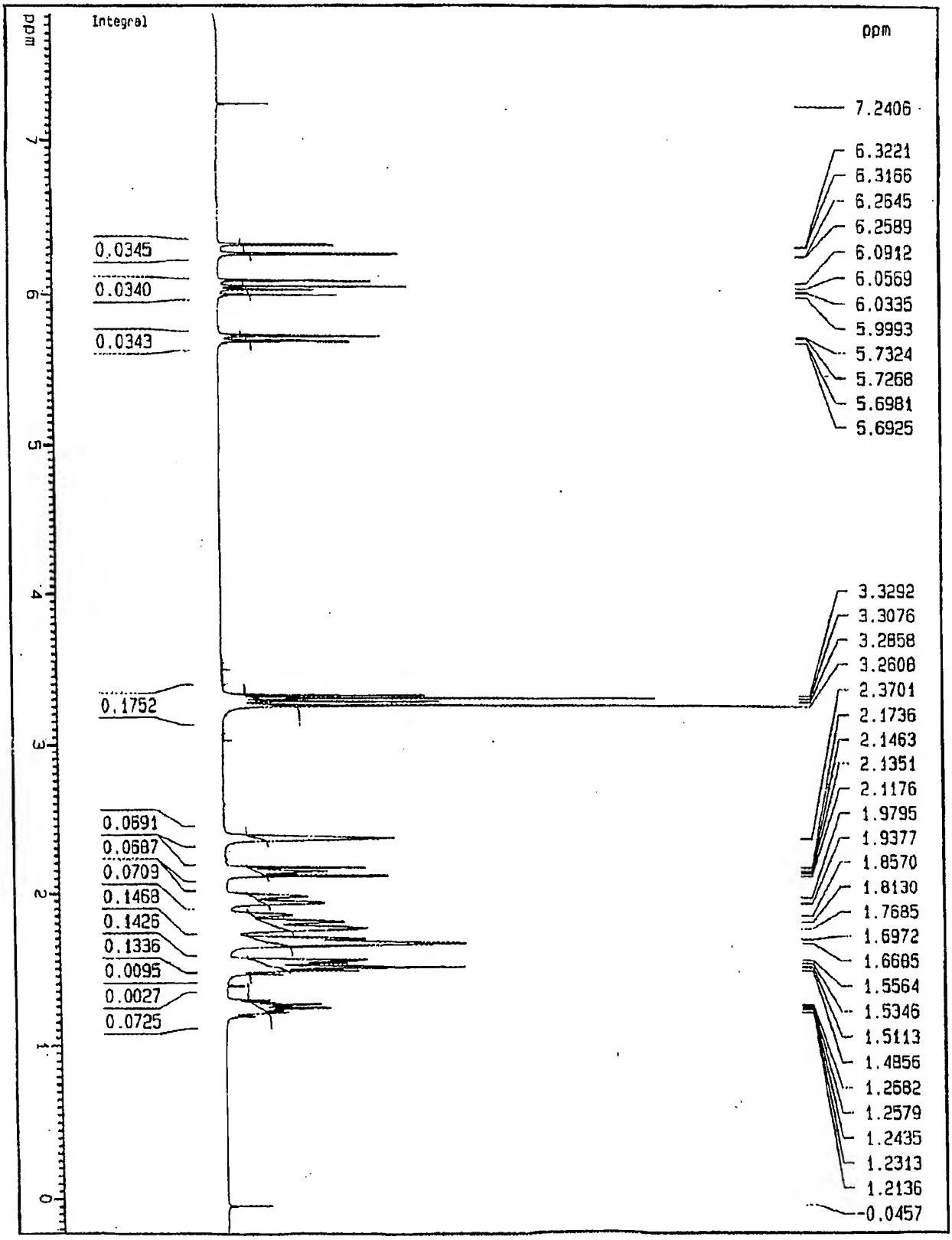
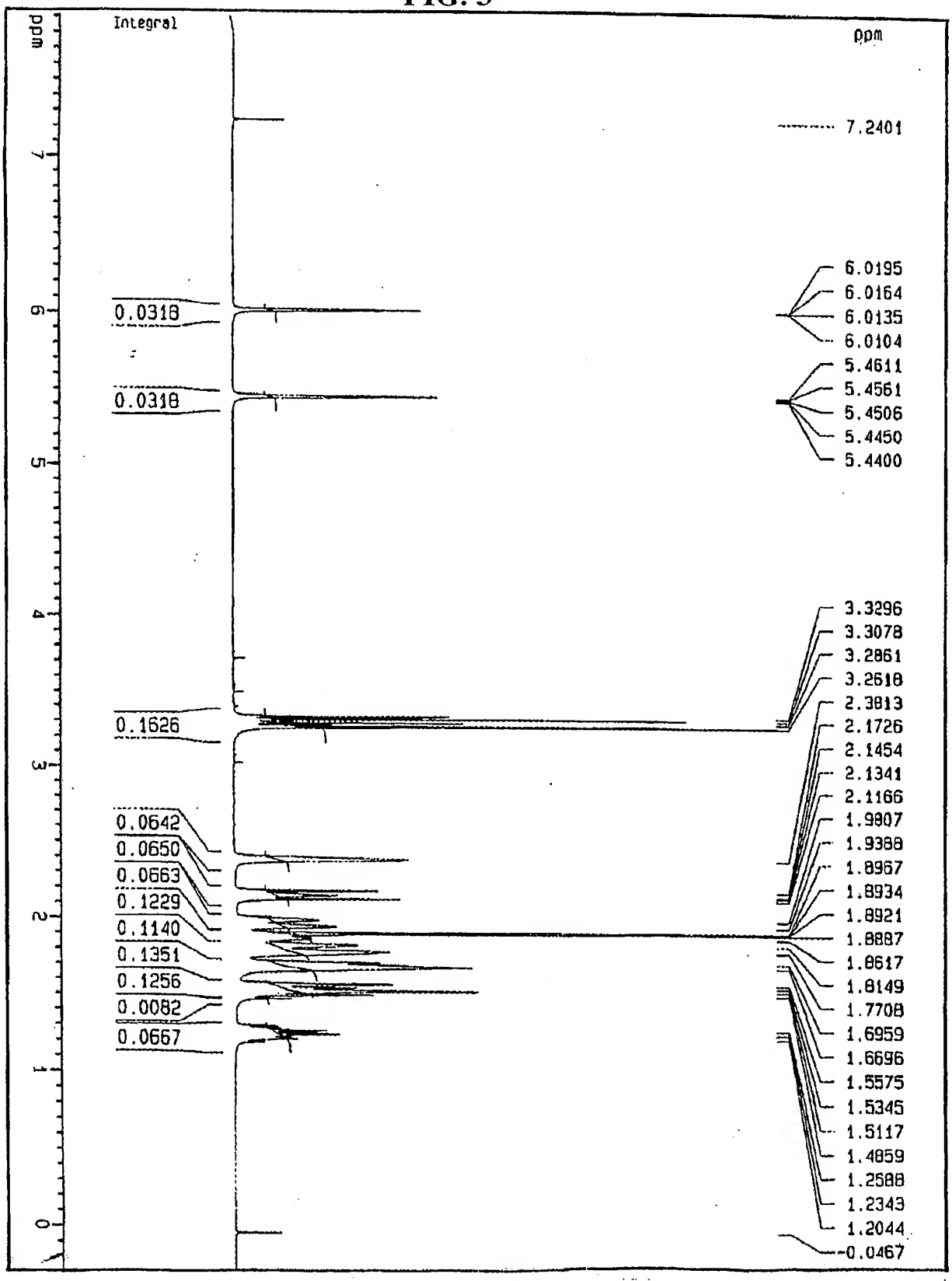


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR03/01151

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C07C 69/54, 67/03, G03F 7/039

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C, G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and Applications for inventions since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
STN(REG,CA)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2001- 81855 A(Chem Search Corp.) 29 Aug. 2001 see claim 1-3	1-5
X	US 6222061 B1(Chem Search Corp.) 24 Apr. 2001 see column2 line45- column3 line10	1-5
X	EP 1127870 A1(Shipley Co. Llc) 29 Aug. 2001 see page3 line35-page4 line 23, page6 Reaction scheme1-5	1-5
X	EP 1020767 A1(Sumitomo Chemical Co. Ltd.)19 Jul. 2000 see example2	1-5
X	US 6013416 A(Fujitsu Ltd.) 11 Jan. 2000 see column27 chemical formula(X X X)	1-2

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23 JULY 2003 (23.07.2003)	24 JULY 2003 (24.07.2003)

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	KANG, Jeon Kwan Telephone No. 82-42-481-5553

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR03/01151

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